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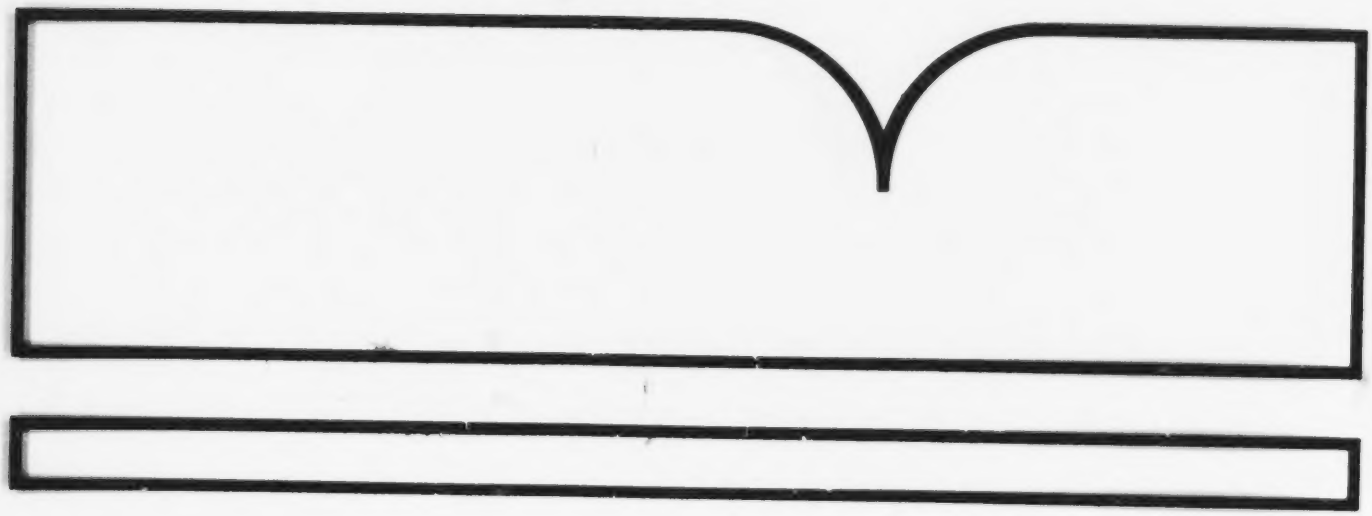

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PREPARATION AND EVALUATION OF NEW SORBENTS FOR ENVIRONMENTAL MONITORING

VOLUME II

Synthesis and Quality Control Testing of Sorbents for Air Monitoring

by

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16. ABSTRACT

Sixty-one different polyimide sorbents were prepared for evaluation as sorbents for the collection of vapor-phase organics in ambient air. Laboratory tests were applied to evaluate their properties as sorbents and to develop a data base to examine relationships between chemical structure and physical properties.

A tiered level-of-effort testing was applied. The Level I procedure sorted the polymers according to specified desired properties; Level II testing provided information for selecting the most promising polymers for trapping of vapor-phase organics and generated the chemical data base relating chemical and physical sorbent properties, and Level III experiments provided a confirmation of the physiochemical properties of the sorbent. Thermodynamic properties and correlations between chemical structure and physical properties were made for four of the more promising polyimide sorbents and compared to Tenax GC, the reference sorbent.

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SECTION 1

1.0 SYNTHESIS OF POLYIMIDE SORBENTS

The synthesis of polyimide sorbents is outlined for one representative polyimide derived from pyromellitic dianhydride (PMDA) and 2,6-dichloro-p-phenylene diamine. Other polyimides are synthesized correspondingly.

1.1 MATERIALS

1.1.1 Source of Materials

Polymerizations are carried out in tetrahydrofuran (THF) of HPLC grade (glass distilled). For the precipitation of the poly(amide-acid) HPLC grade chloroform or diethyl ether is used. The latter is also used for Soxhlet extraction of the poly(amide-acid) preceding the cyclodehydration step. Several sources for HPLC grade solvents are available.

A very pure grade of PMDA is obtained from Tridom/Fluka.

The availability of different diamines depends on their chemical structure. 2,6-dichloro-p-phenylene diamine is obtained from Pfaltz and Bauer.

1.1.2 Purification and Purity Criteria of Materials

1.1.2.1 Solvents

Water traces contained by the solvents are removed by storing over freshly dried molecular sieves (Davison Chemical, Grade 564, 8-12 mesh beads, 0.3 nm pore size). No further purifications were undertaken.

1.1.2.2 Dianhydride

The PMDA was recrystallized from acetic anhydride after one hour reflux under normal pressure. The crystallized PMDA was filtered under exclusion of humidity and then dried at ambient temperature under vacuum (about 7Pa) for 16-18 hr. Further handling was performed inside a glove bag.

1.1.2.3 Diamine

The diamine is first recrystallized from methanol and then dried at ambient temperature under vacuum (about 7Pa) for 16-18 hr. The recrystallized material is then purified by sublimation. Purity determination of the sublimed material by differential scanning calorimetry should reveal a purity of 99.96 mol-%.

1.2 SYNTHESIS OF POLY(AMIDE-ACID) PRECURSOR

1.2.1 Description of Polymerization Equipment

The polymerization equipment consists of a 2 liter cylindrical reaction flask equipped with a water jacket and a three-neck lid providing access for nitrogen inlet, stirrer, and solvent inlet. The solvent (THF) is stored over molecular sieves in a 2 liter bottle which carries a 250 ml buret and a nitrogen inlet. Contaminations by sealing materials is avoided by using Teflon® sleeves on all joints and Teflon needle valves for the buret.

The assembled equipment is connected to the nitrogen line by means of a three-way valve which also permits access to a rotary oil pump for initial evacuation. The nitrogen is dried by passing through a column (1 m × 6 cm) filled with silica gel. The reaction temperature is controlled with a circulating thermostated water bath.

1.2.2 Polymerization Procedure

The assembled reaction flask connected to the solvent buret is first evacuated and then filled with nitrogen. Under nitrogen purge the solvent buret is disconnected and a weighed amount of diamine is added to the reaction flask. After reconnection of the solvent buret a measured amount of THF is added. The stirrer is started and the diamine is allowed to dissolve. Under nitrogen purge the solvent buret is finally disconnected and a stoichiometric amount of PMDA is added. During the addition of both components the circulating water bath is at ambient temperature (20-22°C).

The required reaction conditions strongly depend on the reactivity of the diamine and consequently, on its chemical structure. With the rather unreactive 2,6-dichloro-p-phenylene diamine a reaction temperature of 58°C and a reaction time of 18 hr has been found to be necessary. Highly reactive diamines such as tetramethylbenzidine polymerize at ambient temperature in 2-3 hr.

1.2.3 Isolation of the Poly(amide-acid) Precursor

Most of the diamines polymerize heterogeneously in THF. Nevertheless it advantageous for further handling to use a precipitant such as chloroform or diethyl ether at the end of the polymerization reaction.

The precursor polymer is then filtered through a Teflon® coated glass fiber filter (Bel-Arts Products) and transferred to a Soxhlet for extraction with diethyl ether for 18-20 hr.

1.2.4 Inherent Viscosity Determination

Two samples are taken for the determination of the inherent viscosity of the poly(amide-acid) precursor, one before and one after ether extraction. Viscosities are determined in dimethylacetamide at 30°C with an Ubbelohde viscometer at a concentration of 0.5 g/dl.

1.2.5 Milling and Sieving

Poly(amide-acids) prepared under heterogeneous polymerization conditions are usually obtained in form of small particles suitable for the cyclodehydration step. Particles larger than 500 μm (35 mesh) are removed by sieving and are broken up by mortar and pestel.

1.3 CYCLODEHYDRATION OF THE POLY(AMIDE-ACID) PRECURSOR

1.3.1 Thermal Treatment

The cyclodehydration of the poly(amide-acid) is performed with a rotary evaporator under vacuum (about 7Pa). The polymer resulting after the milling and sieving steps is placed into a round bottom flask which is slowly rotated at about 20-30 rpm. About one third of the flask is submersed in a silicone oil bath which is gradually heated to 230°C. At this temperature the heat treatment is continued for 4-5 hr.

1.3.2 Final Sieving

The polyimide sorbent obtained after thermal treatment is separated into three size fractions 200-500 μm (70-35 mesh), 100-200 μm (140-70 mesh), and smaller than 100 μm (140 mesh) by using a stack of corresponding standard sieves.

2.0 STEP-WISE TESTING PROCEDURE FOR SORBENTS

The close analogy between air sampling with sorbent cartridges and gas chromatographic frontal analysis is the theoretical background for the extensive use of standard gas chromatographic methods for characterizing sorbents for environmental monitoring.[1,2,3]

The outlined testing procedure is designed only to confirm batch-to-batch synthetic reproducibility of a polymeric sorbent, and serves only as quality control and assurance for resynthesis of a sorbent. It is assumed that the polymeric sorbent has already been subjected to rigorous testing prior to its selection for use in ambient air sampling.

2.1 Analytical Procedures

2.1.1 Volatile Background of Sorbent

Glass columns (0.914 m × 2 mm i.d.) are rinsed with 100 mL each of distilled water, methanol and methylene chloride and dried under vacuum. The columns are filled with the sorbent (35/60 mesh) using tapping/suction. The column is weighed before and after filling to determine the amount of polymer packing. The physical characteristics of the polymers are observed and recorded. After conditioning the columns overnight at 300°C under helium flow (20-25 mL/min), temperature programmed gas chromatography (GC) is performed using a detector sensitivity of 2×10^{-11} AFS.

Gas chromatographic parameters:

Septum: Pyrosep with overnight thermal conditioning

Carrier gas: helium (20-25 mL/min)

Mass flow controller: Matheson Model 8240

Detector temperature: Flame ionization, 250°C

Injector temperature: 130-150°C

Temperature program: 50°C initial

50°C-275°C at 8°C/min

The volatile background of conditioned sorbents is evaluated by temperature programmed GC. From the chromatogram, quantitative information is extracted. The inflection point in the tracing defines the maximum rate of volatilization of organic compounds from the polyimide sorbent. A tangent at this point is drawn and the $tg\alpha$ is calculated (see Fig. 1):

$$\text{Max } \mu V/\text{sec} = A/B$$

$$A = \frac{a}{fsd} \times 10^3 \times \frac{\text{sensitivity}}{10^{-12}} \times \text{att} \qquad (\mu V)$$

$$B = \frac{b}{chs} \times 60 \qquad (\text{sec})$$

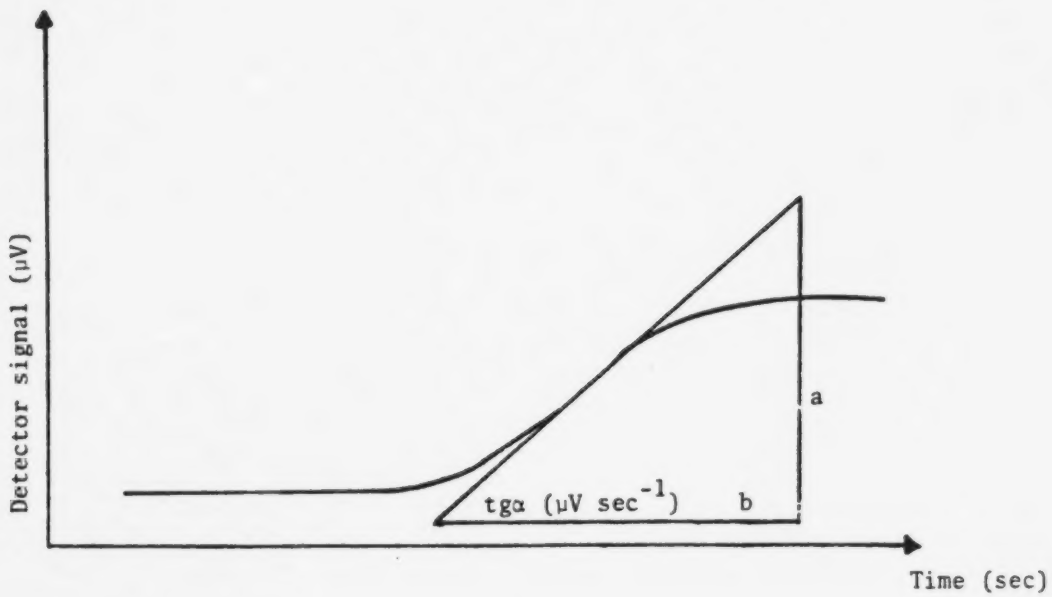

Figure 1. Evaluation of the maximum value of detector signal variation.

where:

a = from Fig. 1, cm,

fsd = full scale deflection of the recorder, cm,

10^3 (to convert 1 mV fsd to uV),

sensitivity = 10^{-11} amp/mV,

10^{-12} = maximum sensitivity of the electrometer, amp/mV,

att = attenuation to the recorder,

b = from Fig. 1, cm,

chs = chart speed, cm/min.

2.1.2 Retention Volumes for Test Substances in Temperature Programmed Gas Chromatography

Retention volumes for a group of test substances are determined using the GC parameters listed above. The test substances used are given in Table 1.

The GC parameters for determining water retention are as follows:

Carrier gas: helium (20-25 mL/min)

Injector temperature: 220°C

Detector: Thermal conductivity, 260°C

Filament temperature: 340°C

Oven temperature: ~120°C isothermal

The test substances are injected as diluted (in air) vapors. Approximately 20 μL of the neat liquid is injected into a 125 mL pierce vial sealed with teflon lined rubber septums. Five and 50 μL samples of gas are removed from the vials with gas tight Hamilton syringes and injected onto the column containing the sorbent.

2.1.3 Theoretical Plates (N)

The retention times and base peak widths are measured on the chromatograms generated for the compounds in Table 1 run at one selected isothermal condition. The theoretical plates are calculated using the relationship:

$$N = 16 \left(\frac{t_R}{w}\right)^2$$

t_R = retention time of the peak, min

w = base width of the peak, min

Table 1. TEST SUBSTANCES EMPLOYED FOR DETERMINING RETENTION CHARACTERISTICS

Compound	B.P. (°C)	Amounts Injected[a]
Benzene	80.1^{760}	175 and 878
Ethanol	78.5	158 and 789
Methyl ethyl ketone	79.6^{760}	161 and 805
Nitromethane	100.8^{760}	227 and 1,137
Pyridine	115.5	196 and 982
C_7, C_8, C_9, C_{10}, n-alkanes	98.4^{760} 125.7^{760} 150.8^{760} 174.1^{760}	146 and 730
Acetonitrile	81.6	157 and 786
1,2-Dichloroethane	83.5^{760}	247 and 1,235
Vinyl chloride	-13.37^{760}	182 and 910
Water	100	200 and 1,000

[a] 5 and 50 µl were injected containing these nanogram quantities.

2.1.4 Peak Asymmetry Factor

Using the chromatograms developed under Section 2.1.3, three test compounds are selected for the calculation of the asymmetry of peaks. The three compounds are ethanol, acetonitrile, and n-octane, representing polar and nonpolar substances. The peak asymmetry factor is calculated as follows:

$$PAF = \frac{B}{F} \times 100$$

where B and F is measured at one-tenth of the peak height (Fig. 2).

2.1.5 Background Determination by Thermal Desorption High Resolution Gas Chromatography

Glass cartridges (50 mm × 6 mm OD) filled with the sorbent are desorbed 4-5 hrs at 250°C, under helium flow, in a thermal desorption unit. Before background evaluation, sorbent cartridges are again desorbed for 2 hrs at 270°C, under helium flow (10 mL/min), directly in the thermal desorption unit. Without cooling the cartridge, the desorbing compounds are trapped cryogenically (-190°C) in a nickel cryofocussing trap for 10 minutes, then injected by flash vaporization onto a fused silica capillary. The analysis parameters are given in Table 2.

All chromatographic runs are performed at the same overall sensitivity of the system (10^{-11} amp · mV). The integrated area are divided in two parts, for the peaks with retention times less than and greater than 15.00 min. From the integrated area, a value is derived for comparison purposes, using the relationship:

$$B = \frac{\text{Area} \times \text{Sens.} \times \text{Att.}}{10^{-12}} \times \frac{10^{-6}}{G} \quad (10^{-6} \text{ area counts/g})$$

where:

B = background,

Area = integrated area for all peaks with retention times greater or less than 15.00 min, arbitrary units,

Sens. = electrometer sensitivity, amp × mV,

Att. = electrometer output attenuation,

G = weight of the sorbent in cartridge.

2.1.6 Surface Area Measurements

Mercury intrusion porosimetric technique is employed for determining

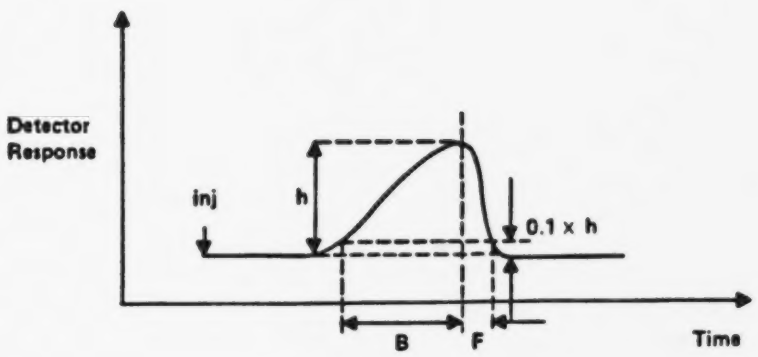

Figure 2. Peak asymmetry factor calculation.

Table 2. THERMAL DESORPTION HIGH RESOLUTION GAS CHROMATOGRAPHIC PARAMETERS

Parameter	Setting
Thermal Desorption Unit	
Temperature	270°C
Desorption time	10 min
He purge flow	10 mL/min
Cryofocussing trap	-190°C to 250°C in 4.5 min
Column	
Fused Silica, 50 m, wide bore	SE-54
Temperature	0 to 250°C @ 4°C/min, 250°C/10 min
He carrier flow	0.5 to 0.6 mL/min

the sorbents surface area (m^3/g) for particles of 35/60 mesh.

2.2 Data Analyses

2.2.1 Volatile Background and Other General Characteristics of Sorbent

The following characteristics are noted:

(a) density (g/ml) - apparent density of the sorbent is determined by dividing the weight of sorbent in the GC column by the column volume. Batch-to-batch variation in density should be approximately ±20 percent relative standard deviation.

(b) weight loss - after conditioning of the sorbent column up to 8% weight loss may be experienced.

(c) volatile background - the volatile background as measured by temperature programmed GC should be <2.5 μV/sec.

2.2.2 Retention Volumes

Replication of retention volumes should be ±15 percent relative standard deviations from one batch to another of sorbent.

2.2.3 Theoretical Plates

The number of theoretical plates is important, because a direct relationshop between collection efficiency and the number of theoretical plates for a substance does exist, which is expressed by the Raymond-Guiochon relationship:

$$BV = V_R \left(1 - \frac{2}{\sqrt{N}}\right)$$

where:

BV = breakthrough volume, volume units;

V_R = retention volume for the samples substance, volume units;

N = number of theoretical plates for samples substance.

The theoretical plate number (N) should be, as a minimum, about 1,000 and ±15 percent relative standard deviations from batch-to-batch of sorbent is deemed acceptable.

2.2.4 Peak Asymmetry Factor (PAF)

PAF values of >65% are satisfactory.

2.2.5 Background of Sorbent Cartridge

The background of the sorbent cartridge should be <0.5 (area counts × 10^{-6}/g) and <0.3 for the first and last 15.0 min, respectively, of a GC run.

2.2.6 Surface Area

Surface area values should be ±15 percent relative standard deviation from batch-to-batch.

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